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OFFICE OF
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MEMORANDUM

SUBJECT: Review of Surface Water Monitoring of Mesotrione (MRID 47244503)

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Attached please find EFED's review of Syngenta's report on their monitoring study for mesotrione in surface water (MRID 47244503). Syngenta describes their submission as proactive; it is not associated with any request and it is not specific to any action currently under consideration.

The study analyzes raw and finished water samples collected from 2005 – 2007 at Community Water Systems included in the Atrazine Monitoring Program. In raw water, the study found mesotrione concentrations of up to 2.4 ppb with primary dissipation times of one to several weeks and low levels (≤0.5 ppb) persisting for several weeks beyond that. Sampling was conducted in the Midwest, primarily in Illinois, Indiana, and Ohio, and in those areas is representative of use on corn, the only registered use at the time of sampling.

There were no detections of mesotrione in finished water sampled in the same locations at the same time, suggesting that the water treatment methods used are effective at removing mesotrione. In addition to the monitoring study, a laboratory study of the effects of chlorination on raw water samples is attached as an appendix to the main document. Based on preliminary review, that study demonstrates that upon addition of chlorine, mesotrione is rapidly degraded to the major degradate MNBA. That study will be reviewed formally in a separate document.

On review, EFED concludes that the study is unacceptable but upgradeable. The report does not include any information on analytical methods or on storage stability characteristics. Samples were stored up to 18 months, so this is an important gap. If satisfactory information is submitted to address these issues, the study would be upgraded to supplemental. If upgraded, the results of the study can be incorporated into drinking water assessments for mesotrione. Given uncertainties regarding the vulnerability of monitored sites, as described in more detail in the site selection discussion, these data would be used for qualitative characterization. If information is submitted to confirm that the monitoring is sufficiently representative of vulnerable use areas, the data might be used more quantitatively for estimating drinking water concentrations from use on corn, especially for chronic exposure results.

EFED's review of this study used an electronic version of the data submitted under DP Barcode D353725 as well as the original hard copy.

I. BACKGROUND

Mesotrione is a systemic tri-ketone herbicide used in preemergent and postemergent applications for control of annual broadleaf weeds. It is currently labeled for use on corn, and in some registered end use products it is formulated with s-metolachlor and atrazine to broaden the spectrum of controlled weeds. New uses are currently being considered for registration, including uses on asparagus, grasses grown for seed, oats, okra, rhubarb, sorghum (grain and sweet), sugarcane, cranberries, bush and cane berries, flax, millet, and turf.

For use on corn at the maximum annual application rate of 0.43 lb a.i./A, estimated drinking water concentrations (EDWCs) based on Tier I aquatic modeling are 15 ppb for acute exposure and 1.8 ppb for chronic (annual average) exposure (DP Barcode D283823; 8/19/2002). Considering all uses, the Tier I EDWCs are 38.7 ppb for acute exposure and 4.7 ppb for chronic exposure (DP Barcodes D325840, D333402, D333409, D333414, D333419; 1/18/2007). To date, there has been no need for more refined Tier II modeling.

Field and laboratory studies indicate that mesotrione is mobile to moderately mobile with limited persistence in soil and aquatic environments. It is acidic and its fate properties have a strong dependence on environmental pH. Terrestrial field dissipation studies showed dissipation half-lives of 2 to14 days and did not find any residues below 6 inches (DP Barcodes D253844, D259964, D268681; 05/03/01). A small-scale prospective ground water monitoring study also suggests that mesotrione is unlikely to leach to ground water (DP Barcode D352675, D353725; 9/17/08).

Metabolism of mesotrione led to two major degradates: MNBA, formed through aerobic metabolism at up to 60% of applied, and AMBA, formed through anaerobic metabolism at up to 60% of applied. AMBA is somewhat more persistent than mesotrione, but several terrestrial field dissipation studies and prospective ground water monitoring studies have found it to only be present in soils at low levels. MNBA is less persistent and has not been detected in field studies. This monitoring study does not include analysis for the degradates.

II. MATERIALS AND METHODS

Site Selection

The Community Water Systems (CWS) that this study targeted for mesotrione analysis were a subset of the sites sampled in the ongoing Atrazine Monitoring Program (AMP). The AMP includes surface water monitoring at roughly 130 sites which met the criteria for expected vulnerability to atrazine exposure. The criteria were based on past detections of total chlorotriazines (TCT; atrazine, simazine, and their three common chloro-azine metabolites) at levels in exceedance of those agreed upon by EPA and Syngenta for triggering entry into the monitoring program. High TCT detections in these locations indicate vulnerability due to relatively high atrazine usage and/or environmental conditions leading to high surface water runoff potential.

From within this group of CWS, Syngenta selected 108 sites in 2005 from which to analyze raw water samples for mesotrione. Sites were selected based on availability of samples for analysis and on the relative amount of mesotrione use in the sampled location. Of these sites, 88 were in watersheds which were in >50th percentile for mesotrione sales intensity for that year[1] (in lb/A). See Table 1 for use distribution information. Sampling continued in 2006 at 81 of the CWS from 2005 and at an additional 10 sites. Sixty of the sites sampled in 2006 were sampled again in 2007, but there are no use data available for that year. Overall, 50 sites were sampled in all three years.

Table 1. Number of Sampled CWS Sites, Based on Mesotrione Use Intensity.

Year	Use Intensity (lb/A) Percentile				TOTAL SITES
	> 90th	75th – 90th	50th – 75th	< 50th	
2005	16	46	26	20	108
2006	18	44	24	5	91
2007	No data available.				60

Sampling in this study was designed for atrazine and was not targeted to detect mesotrione. Because sites were selected based on atrazine vulnerability, they are not necessarily representative of mesotrione vulnerability as well. Both herbicides are used

[1] These numbers are based on the legend from Figure 1 (p. 10). The text (p. 6) states that 80 sites were in watersheds with >50th percentile use intensity, rather than 88 as is reported in the figure.

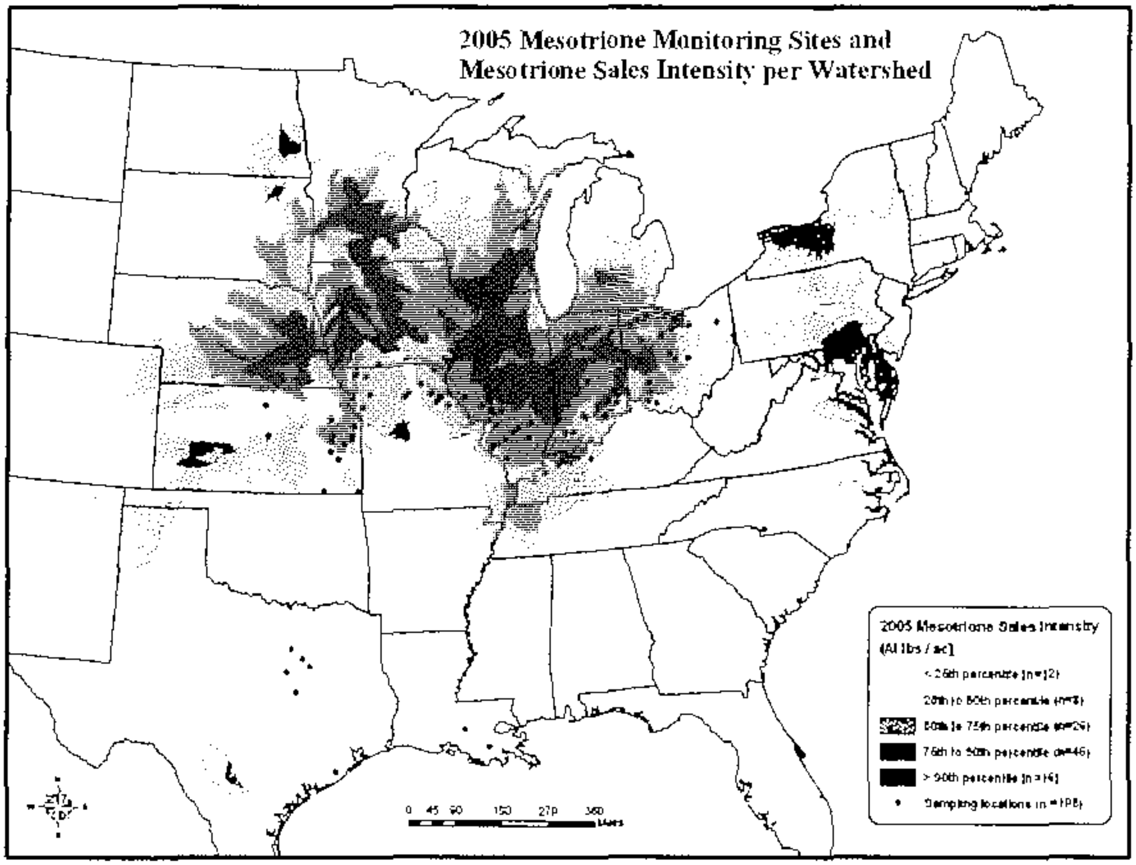
primarily on corn and are sometimes used in conjunction in order to broaden the weed spectrum treated, so the study assumes that mesotrione use, and therefore vulnerability, is correlated with atrazine use. The study includes use data to support this assumption, but uncertainty remains as to what level of mesotrione vulnerability is represented by the sampling pattern.

Mesotrione use maps included in the study report demonstrate that sampling is generally in high use areas (see Figures 1 and 2). However, the sampling only represents a portion of high mesotrione use areas, so there is uncertainty about the potential vulnerability outside of the sampled area. Sampled CWS are located primarily in a narrow band in the Midwest from eastern Kansas through northern Missouri, southern Illinois and Indiana, and into western Ohio. Only a portion of national mesotrione use areas are represented by this sample set. Therefore, although most of the sampled CWS are in watersheds with high use, they are not necessarily representative of exposure vulnerability nationally. For example, although more than 60 of the sites sampled in 2006 are in locations with >75th percentile use intensity, they represent a limited area; ~20 sites are in southwestern Illinois, and another 10 are in a small area of eastern Kansas, while many of the watersheds in the >75th percentile use category are in unsampled areas of eastern Nebraska, Iowa, Minnesota, Wisconsin, and northern Illinois. Additionally, there is use throughout the mid-Atlantic coastal region and the northeastern states, as well as in the southern Mississippi River basin where there is no sampling. Although those areas are generally lower in use intensity, they are also likely to have different environmental conditions that may contribute to vulnerability. A discussion of the vulnerability in use areas where sampling was not conducted would add to the value of this study.

Additionally, no discussion is included of the types of watersheds represented by the sampled sites. The AMP sites were chosen to include samples from large and small watersheds as well as from both river and reservoir systems. The portion of these watersheds sampled for mesotrione is not described.

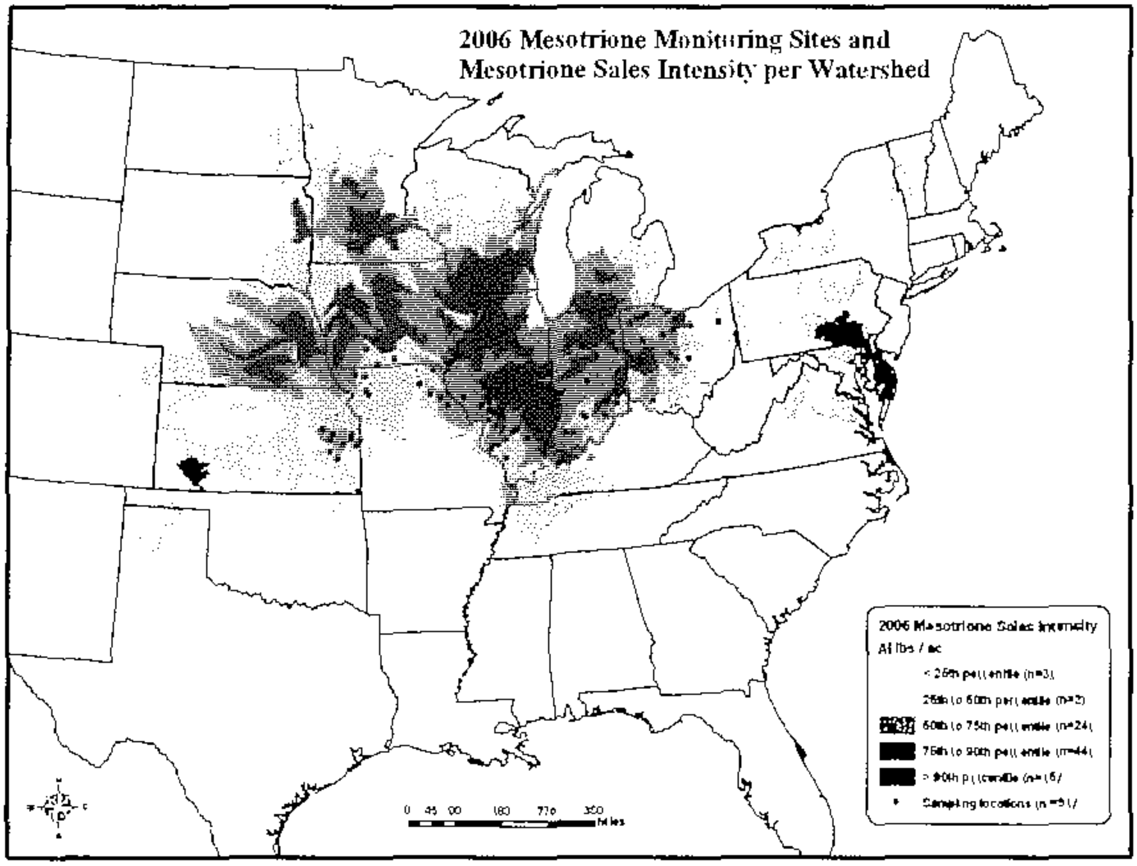
Finished water samples were analyzed for mesotrione at all sites which had detections in raw water samples.

FIGURE 1. Spatial Distribution of 2005 Mesotrione Monitoring Sites Relative to Mesotrione Watershed Sales Intensity.



(from MRID 47244503, p. 10)

FIGURE 2. Spatial Distribution of 2006 Mesotrione Monitoring Sites Relative to Mesotrione Watershed Sales Intensity.



(from MRID 47244503, p. 11)

Sampling Schedule
The study measures mesotrione in samples collected for the AMP in 2005–2007. Atrazine sampling was conducted weekly during the atrazine use season, April to September, and biweekly in the off-season. Samples collected during the peak mesotrione use season were targeted for analysis (April 1–June 30 in 2005 and 2006; April 15–July 15 in 2007). Sampling was later in 2007 because planting was later, due to weather conditions.

In 2005, sampling was less frequent than in subsequent years. On average, 4 samples were collected at each site, and many of these samples were taken in February or March, described by the authors as outside of the peak use period. In 2006 and 2007, samples were taken an average of 7 to 8 times at each site, primarily in the peak use period. Except for 2005, then, samples at most sites were collected every one to two weeks during the peak use period.

At all sites with raw water detections, finished water samples were analyzed as well. At these sites, finished water was analyzed for every sampling event, whether or not there had been a raw water detection on that particular day.

Sampling and Analysis Methods
No information was provided about sampling methods, although the samples were collected as part of the AMP, for which sampling protocols were reviewed by the EPA . Additionally, no information was provided about the analytical methods used, including method description, method validation, procedural recoveries, or other information. The limit of quantitation (LOQ) is reported to be 0.05 ppb, but no detection limit is reported.

No storage stability data were provided. This is an important gap because some samples were stored up to 18 months prior to analysis.

III. RESULTS AND DISCUSSION

Finished Water
None of the 798 finished water samples analyzed for mesotrione had detections above the LOQ (0.05 ppb). The report cites a laboratory study, attached to the report as Appendix 1, indicating that chlorination of raw water is an effective method of water treatment for mesotrione. This chlorination study has not yet been reviewed independently by EFED. In the cited study, chlorine was added to raw water samples fortified with mesotrione. After two hours, $\leq$ 3% of the applied compound remained present as mesotrione with the rest having metabolized to MNBA. At the end of the 24 hour study period, 89% to 108% of the applied material remained present as MNBA. The study was conducted using raw water from the American River in California, described by the authors as a typical drinking water source. There is no discussion of the fate of MNBA in finished water and no sampling for this compound.

Raw Water

Throughout the study period, 2476 raw water samples were tested for mesotrione. Of these samples, 491 (20%) had detections above the LOQ, with detections found at 56 of the 118 sites sampled. The frequency of detections by year and site is presented in Table 2. The study report does not identify the amount of mesotrione use associated with sites where mesotrione is detected and there is no discussion of whether the sites with high or with frequent detections are also sites with the high use intensity.

Table 2. Distribution of mesotrione detections by year and site.

YEAR	TOTAL SAMPLES			TOTAL SITES		
	No. of detections	No. of samples	% detection	No. of sites w/ detections	No. of sites	% detection
2005	43	634	6.8%	22	108	20%
2006	268	1105	24%	50	91	55%
2007	177	738	24%	35	60	58%
ALL	491	2476	20%	56	118	47%

It should be noted that the relatively low number of detections in 2005 is likely due to the fact that the dataset for this year is less robust than the others, rather than due to lower exposure. In 2005, sites were tested less frequently (average of 4 samples per site) and were less representative of high use areas and periods. Approximately 40% of samples from 2005 were collected in areas in the lowest use bracket (<25th percentile by lb/A) or in times outside of the peak use season (in February or March, rather than April through June).

In raw water samples with detections, the annual average and the maximum concentrations in 2005 were 0.22 and 1.2 ppb, respectively, in 2006 were 0.32 ppb and 2.4 ppb, and in 2007 were 0.19 ppb and 1.5 ppb. The highest concentration (2.4 ppb) was detected once at Monroeville, Ohio, on April 24, 2006, and once at Lake Santee, IN, on May 1, 2006. Monroeville appears to be in the 75th – 90th percentile use category based on the submitted use maps, but the category is not clear for Lake Santee.

Fourteen sites had detections of $\geq$ 1 ppb: 1 in Illinois, 1 in Missouri, 6 in Indiana, and 6 in Ohio. Another 13 sites had detections at concentrations $\geq$ 0.5 ppb. Most sites had multiple detections, with 1 to 20 detections per site, and an average of approximately 9. Of the 50 sites that were sampled during all three years, 9 sites had detections each year, although due to the limited data in 2005, this may not be complete.

Monitoring data from sites with detections are presented in Figures 3 and 4, for 2006 and 2007, respectively. In 2006, there are 14 samples with detections above 1 ppb and a number of detections between 0.5 and 1 ppb. These data show few detections early in the season with concentrations jumping to maximum measured levels in late April to early May and then decreasing more slowly through the rest of the season. The highest concentrations are seen in Ohio and Indiana. Many of the detections of >1 ppb were sampled on the same day, May 15. There are several peaks in Indiana later in June. At the end of the monitoring period, with final samples taken between June 12 and June 27, mesotrione was still detected in 31 of the sites, at levels from 0.05 to 0.539 ppb.

Measured concentrations in 2007 are lower, all <0.5 ppb, with a few exceptions. In most sites, detections begin at the end of April and continue through the end of the sampling period with no clear pattern of increase or decline. Eight sites had detections on the final day of sampling, at levels ranging from 0.07 to 0.31 ppb.

Figures 5 and 6 show data from 2006 at several of the individual sites that had concentrations of >1 ppb [2]. 2006 had the most data and the highest detections and so best shows patterns of detection. Figure 5 represents monitoring at both sites that had detections at the highest concentration, 2.4 ppb. At both sites, the maximum concentration was detected early in the season and had decreased to ≤0.1 ppb by the next sampling date, one week later. At the Indiana site, the concentration was high again the following week (1.5 ppb) and then dropped more slowly with concentrations remaining between 0.36 ppb and 0.75 ppb for the final six weeks of the sampling period. In Ohio, measured concentrations were lower and more variable, with the next highest detection 0.83 ppb (June 12, 2008) and ending at 0.13 ppb (June 26, 2006). In the following year, 2007, Lake Santee had no detections out of 13 samples and Monroeville had detections in 6 of 11 samples, ranging from 0.07 ppb to 0.56 ppb.

Figure 6 shows 2006 monitoring results from 4 of the sites with detections of ≥ 1 ppb. Other sites that had high detections for this year but that are not included in the figure generally follow similar trends. At many of the sites monitored in 2006, the highest concentrations were detected on May 15 or 16, suggesting a large precipitation event around this time. Within two weeks, concentrations at three of the four sites had decreased to <0.4 ppb and then dissipation slowed, with only one non-detect over the next month and the remaining samples between 0.07 ppb and 0.28 ppb. At the fourth site, in Indiana, another peak occurred in early June with a concentration of 1.8 ppb, dissipating to 0.54 ppb in the final sample two weeks later.

[2] These figures display data points that were below the LOQ of 0.05 ppb as 0 ppb.

Figure 3. 2006 CWS Monitoring Data (sites with detections)

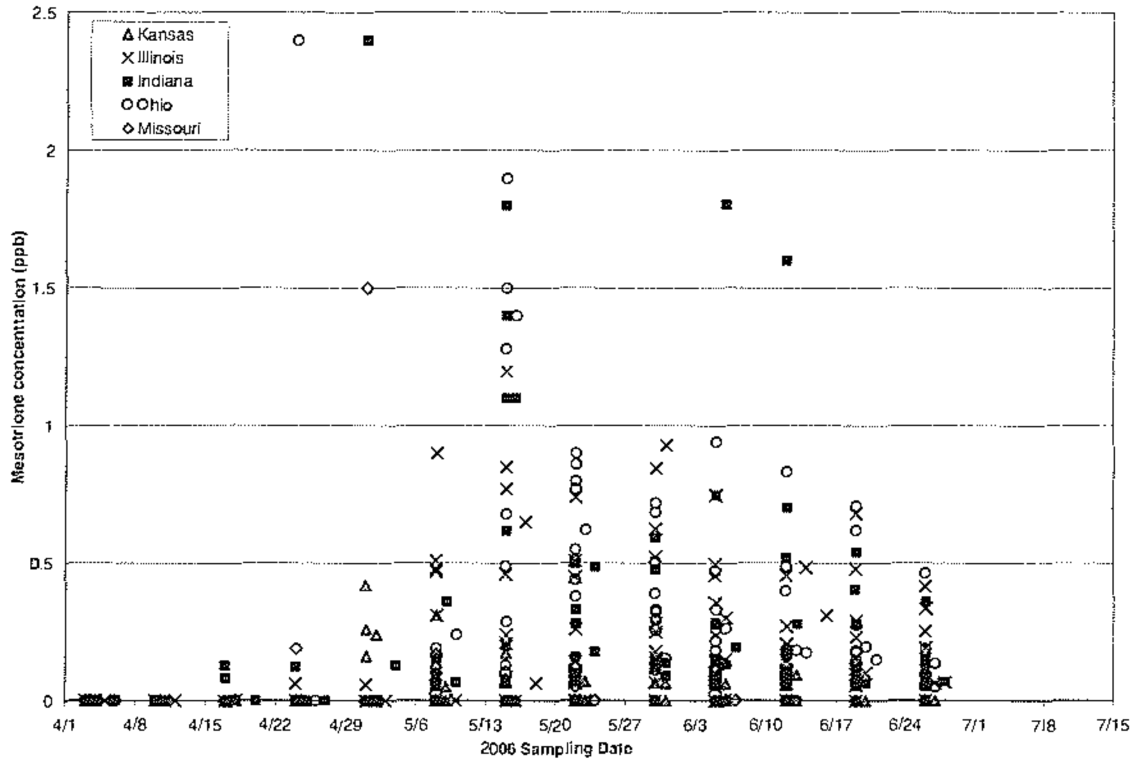


Figure 4. 2007 CWS Monitoring Data (sites with detections)

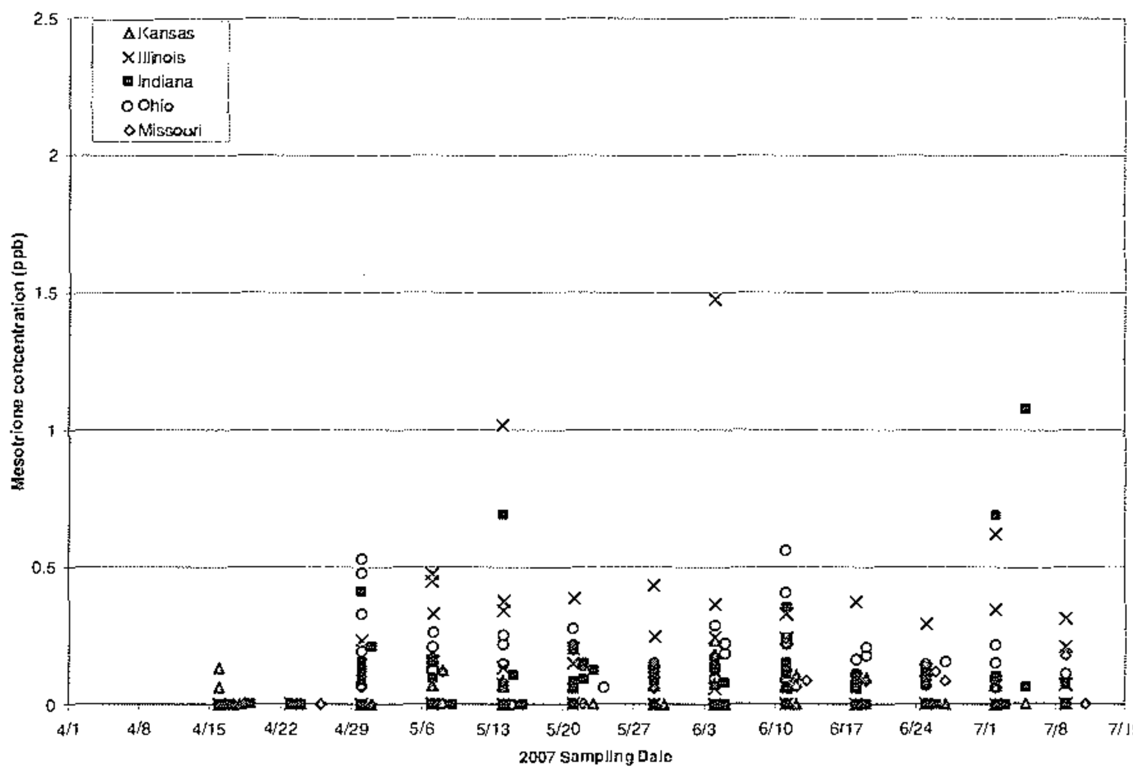


Figure 5. 2006 Monitoring Data at sites with the highest detections (2.4 ppb)

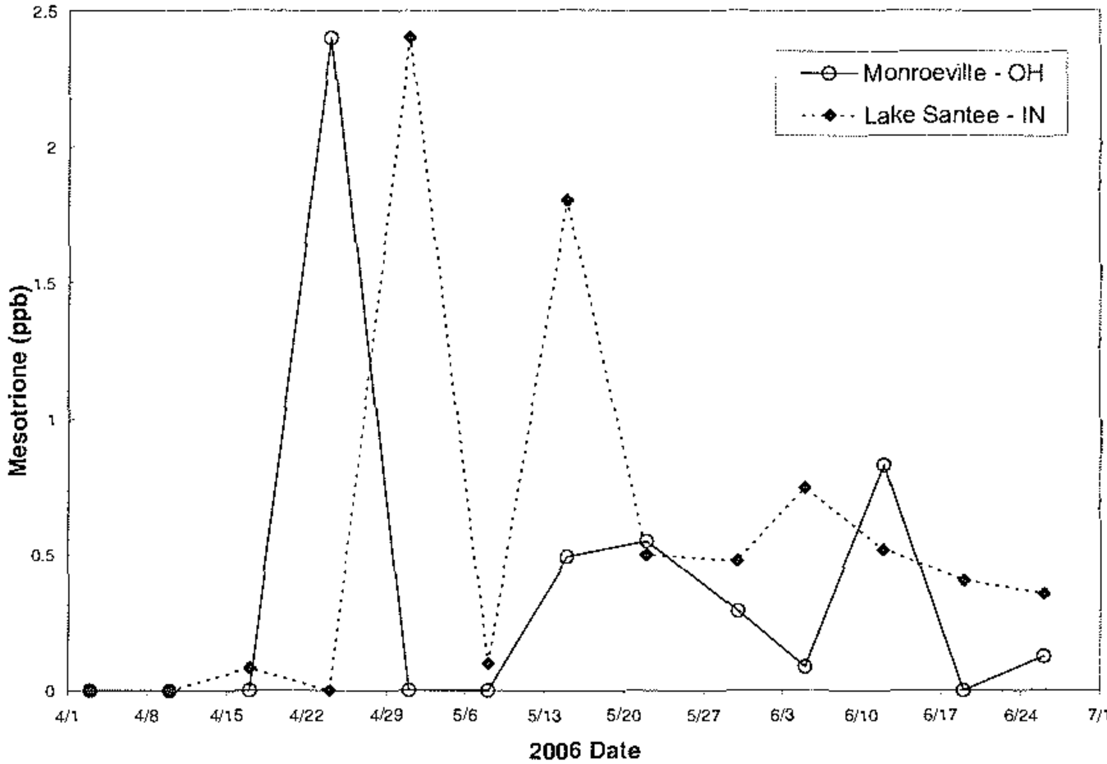
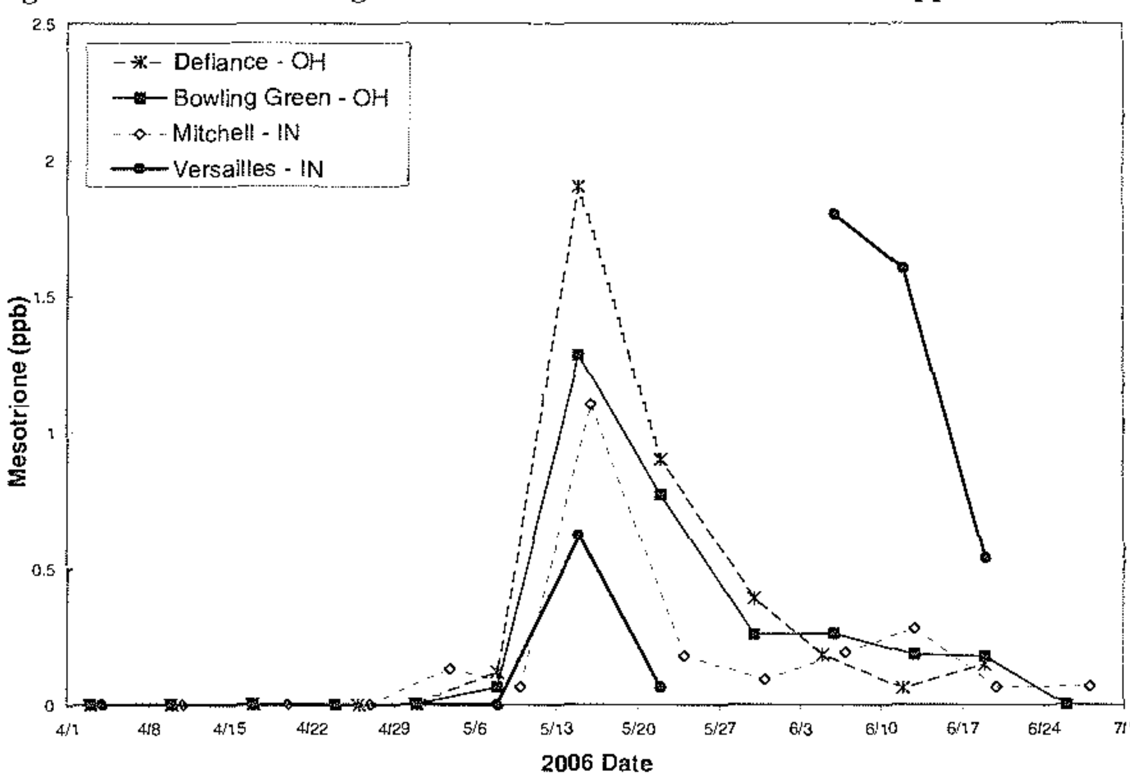


Figure 6. 2006 Monitoring Data at several sites with detections >1 ppb.



IV. CONCLUSIONS

Over a three year sampling period, mesotrione was detected in raw water samples from 56 of 118 CWS sites at concentrations up to 2.4 ppb. Samples were collected primarily in the Midwest, and more than half of the sites were in areas with use intensity in the 75th percentile or greater, although there was no sampling in many other high use areas. Dissipation patterns seen for the higher detections of mesotrione (≥ 1 ppb) show that dissipation primarily occurred within one to several weeks of the peak, with concentrations remaining at lower levels (0.05 ppb to 0.5 ppb) for longer periods. At some sites, detections at these lower levels continued through the end of the sampling period. The fastest dissipation was seen in the samples with the highest concentration, 2.4 ppb. These detections occurred early in the season; slower dissipation was seen at the at the same sites later in the season, perhaps due to more widespread use at that time.

In previous assessments, Tier I aquatic modeling predicted EDWCs from use on corn of 15 ppb for acute exposure and 1.8 ppb for chronic exposure (DP Barcode D283823; August 19, 2002). To date, there has been no need for more refined Tier II modeling. The results of this monitoring study can be used to help characterize EDWCs predicted through modeling. If it is determined that monitoring sites represent the most vulnerable use areas, monitoring results, particularly for chronic exposure, may be used more quantitatively.

Finished water was analyzed at all sites where mesotrione had been detected in raw samples and no detections above the LOQ were found in any samples. This suggests that water treatment methods are effective at removing mesotrione. A chlorination study attached as Appendix 1 tests one system described as a typical river drinking water source. On preliminary review, the study shows rapid conversion of mesotrione to MNBA after addition of chlorine. 24 hours after chlorination, residues were still present as MNBA. The study will be formally reviewed in a separate document.

V. UNCERTAINTIES

Monitoring is not expected to capture peak exposures, due to limited sampling frequency and spatial distribution. Although weekly sampling in widespread areas, as in 2006 and 2007, is valuable in describing potential exposure, there are still uncertainties. The sampling design was not targeted to detect mesotrione exposure and there were large regions of high intensity use where no sampling was conducted. Additionally, these monitoring results represent exposure resulting from the use patterns at the time of sampling. Currently, there are a number of new uses under consideration, including some with widespread use and some with higher application rates than those on corn, and mesotrione use on corn may be increasing, as well.

Vulnerability is determined by environmental conditions as well as by use intensity, a factor that is not discussed in the study report. For example, given that it does not appear that use decreased over the study period, the detection of higher concentrations in 2006 than in 2007 demonstrates the importance of weather conditions. In particular, the number of high detections on the same day in 2006 suggests that a single precipitation event can substantially affect exposures, although rainfall data were not included to confirm this. A similar atrazine sampling program, conducted for assessing ecological impacts rather than drinking water impacts, found that environmental conditions including soils and precipitation could be as important as use intensity in resulting exposure. Consideration of whether higher detections were found in areas of more intense use, during precipitation events, or due to other factors affecting vulnerability was not discussed.

The monitoring study did not analyze for major degradates AMPA or MNBA in raw or finished water samples. Laboratory fate studies for mesotrione suggest that MNBA is less persistent than mesotrione, and in several terrestrial field dissipation studies and a prospective groundwater monitoring study, no MNBA was detected. The chlorination study demonstrates, however, that MNBA is a major byproduct of disinfection and there is no discussion of the fate of this degradate.

Additionally, the analytical methods were not reported and storage stability information was not included, important given that some samples were analyzed as much as 18 months after collection.